# (19) World Intellectual Property Organization International Bureau





# (43) International Publication Date 16 May 2002 (16.05.2002)

## **PCT**

# (10) International Publication Number WO 02/38703 A1

(51) International Patent Classification<sup>7</sup>: 47/24, C07C 2/02, 7/20

C10G 47/02,

(21) International Application Number: PCT/US01/45509

(22) International Filing Date: 24 October 2001 (24.10.2001)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 09/708,067 8 November 2000 (08.11.2000) U

(71) Applicant: CHEVRON U.S.A. INC. [US/US]; 2613 Camino Ramon, 3rd floor, San Ramon, CA 94583 (US).

(72) Inventor: O'REAR, Dennis, J.; 40 Upland Drive, Petaluma, CA 94952 (US).

(74) Agents: ZAVELL, A., Stephen et al.; Chevron Corporation, Law Department, P.O. Box 6006, San Ramon, CA 94583-0806 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: MANUFACTURE OF LUBRICANTS FROM FISCHER-TROPSCH SYNCRUDE

(57) Abstract: A process for manufacturing a lube base stock, and the lube base stock produced by the process, is disclosed. The method involves converting a light hydrocarbon feedstock into syngas, converting the syngas to hydrocarbon products via Fischer-Tropsch synthesis, and isolating a predominantly 650 °F- containing fraction (preferably including predominantly C<sub>5-20</sub> hydrocarbons) and a predominantly 650 °F+ containing fraction. The 650 °F- containing fraction can be converted to distillate fuels, either at the site where the Fischer-Tropsch synthesis occurs, or at a different location. The 650 °F+ containing fraction is converted to lube base stocks, preferably at a site different from the site where the Fischer-Tropsch synthesis occurs. Petroleum products with boiloing points in the 650 °F- or 650 °F+ ranges can be blended with the corresponding 650 °F- or 650 °F+ containing fractions. Portions of the syngas generator, Fischer-Tropsch synthesis reactor and/or equipment used for isolating the 650 °F- or 650 °F+ containing fractions can be disassembled, transported to another location, and used in the other location. Ideally, the parts can either be reassembled at the other location, or combined with other parts and assembled into a syngas generator, Fischer-Tropsch synthesis reactor and/or equipment for isolating various product fractions.

WO 02/38703 A1

## Manufacture of Lubricants from Fischer-Tropsch Syncrude

#### Field of the Invention

This invention is generally in the area of Fischer-Tropsch synthesis and, more particularly, relates to an efficient method for preparing lubricants from Fisher-Tropsch syncrude.

## Background of the Invention

The conversion of natural gas to salable products requires a large amount of capital.

Fischer-Tropsch synthesis, which converts methane to higher molecular weight hydrocarbons, is currently considered one of the most economical processes. However, the natural gas feedstock is often located in remote locations, where it is more expensive to construct commercial plants than it is in industrialized nations.

Accordingly, it is desirable to use the minimum capital investment in remote locations. One way to keep costs down is to hydroprocess the Fischer-Tropsch products at commercial refineries far from where the Fischer-Tropsch synthesis is performed.

The products of Fischer-Tropsch synthesis are mostly linear hydrocarbons that often include high melting point wax. A C<sub>5</sub>+ product stream which is solid at room temperature, commonly referred to as "syncrude," can be isolated. In the Mossgas facility in South Africa and Shell's facility in Malaysia (both developed sites with low to moderate capital costs), methane is converted to Fischer Tropsch syncrude which is refined at the site to finished salable products. The syncrude can be transported to commercial refineries for hydroprocessing, for example by hydrocracking, hydroisomerization and hydrotreatment, to provide products with desired properties.

Methods for transporting Fischer-Tropsch derived syncrude from a remote site to a commercial refinery are known in the art (See, for example, U.S. Patent Nos. 5,968,991; 5,945,459; 5,856,261; 5,856,260 and 5,863,856). One approach has been to isolate a C<sub>20-36</sub> syncrude and ship this composition as a solid. A limitation of this approach is that it is difficult and expensive to transport solids, because it requires expensive forming, loading and unloading facilities.

1

25

30

5

10

15

Other approaches have focused on transporting syncrude, or a syncrude which has been partially refined at the remote site to convert some of the linear hydrocarbons into iso-paraffin and thus generate a syncrude which is liquid at near ambient temperature. One approach to transporting syncrude in the liquid state involves partially dewaxing the syncrude to form a pumpable liquid (See, for example, U.S. Patent No. 5,292,989). However, this dewaxing may require the construction of facilities which are expensive and difficult to operate in remote locations.

Another approach involves transporting the syncrude as a molten wax. This transportation method does not require the forming, loading and unloading facilities needed to transport solids, or the dewaxing facilities needed to convert the syncrude into a product that is liquid at room temperature. A limitation of this approach is that Fischer-Tropsch syncrude includes a sufficient quantity of volatile hydrocarbons to cause it to exceed conventional vapor pressure specifications if the syncrude were shipped at a temperature at which it is molten.

15

20

25

30

10

5

Regardless of the shipping method, the cost of constructing plants for converting the methane and shipping the syncrude are relatively high. It is therefore desirable to generate products that are valuable enough to justify the expense. The Fischer-Tropsch products are generally linear hydrocarbons, which can be converted into a variety of commercial products, such as jet fuel, diesel fuel, and lube base stocks. Lube base stocks are the most valuable of these products. Accordingly, it would be desirable to develop cost efficient methods for converting natural gas to lube base stocks via Fischer-Tropsch synthesis. U.S. Patent No. 4,965,475 discloses a method for converting natural gas to Fischer-Tropsch wax, shipping the wax to a developed location (as a solid), and refining the wax into a lube base stock. However, there are several commercial considerations associated with converting methane to lube base stocks which are not addressed by the '475 patent.

The lifetime of the natural gas asset needs to be considered. Gas assets are typically classified as either dry gas or associated gas. Dry gas is gas from a reservoir that typically does not contain crude oil or natural gas condensate. Associated gas is gas from a reservoir that accompanies crude oil. The gas assets may be depleted quickly in comparison to the capital depreciation time for the plant to process the gas.

This is particularly true for associated gas, which typically has a lifetime of 5-10 years.

If the plants are built on-site to process the gas, the gas field can be exhausted before the facility has recovered the invested capital. Further, current Fischer-Tropsch facilities are typically small (about 10,000 BPD) and the most cost efficient lube facilities would use much more feed, as the cost of production decreases as the plant grows larger. Also, lube base stocks derived from Fischer-Tropsch syncrudes tend to have different physical and chemical properties than current lube base stocks.

5

10

15

20

25

30

It would be desirable to develop processes that are economically viable given the short lives of typical gas assets, can handle more than 10,000 BPD of feed, more preferably greater than 25,000 BPD or feed, and most preferably, greater than 50,000 BPD of feed, and can increase output over time with a minimum of additional capital expense. The present invention provides such a process.

### Summary of the Invention

A process for manufacturing a lube base stock, and the lube base stock produced by the process, is disclosed. The method involves converting a light hydrocarbon feedstock into syngas, converting the syngas to hydrocarbon products via Fischer-Tropsch synthesis, and isolating a predominantly 650°F- containing fraction (preferably including predominantly C<sub>5-20</sub> hydrocarbons) and a predominantly 650°F+ containing fraction either derived from, or, preferably, directly from the Fischer-Tropsch product stream. The including predominantly C<sub>5-20</sub> hydrocarbons (and predominantly C<sub>5-20</sub> fraction) is a fraction that includes at least 80%, preferably at least 85%, and more preferably, greater than 90% by weight of products that boil in the range of between 50 and 700°F. The 650°F- containing fraction can be converted to distillate fuels, either at the site where the Fischer-Tropsch synthesis occurs, or at a different location. The 650°F+ containing fraction is converted to lube base stocks, preferably at a site different from the site where the Fischer-Tropsch synthesis occurs through transportation to and receiving at said different site. The fractions can be converted to distillate fuel and lube base stocks at the same site or at different sites. Fractions from multiple sites can be combined for conversion.

The fractions are preferably transported by methods described in co-pending application entitled "Method for Transporting Fischer-Tropsch Products" filed concurrently herewith and incorporated herein by reference in its entirety. In particular the

fractions when transported for hydroprocessing, preferably have true vapor pressures at the transportation temperature of less than about 15 psia, preferably less than 11 psia. The fractions are both preferably at least partially liquid at the transportation temperature. The fractions can be transported using any commonly used means of transportation, including marine tankers, rail cars, pipelines, trucks, barges and combinations thereof. A preferred means of transportation is a marine tanker and, more preferably, each transportable fraction is either transported in a separate marine tanker or in separate zones within the same tanker. When transported by rail, truck, or barge, each fraction is preferably transported either in a separate rail, truck or barge, or in separate zones for each fraction within the same rail, truck or barge.

5

10

15

20

25

30

The conversion of the 650°F+ containing fraction to lube base stocks will involve dewaxing, which may be catalytic dewaxing, solvent dewaxing or combinations thereof. The conversion of either fraction to final products may also include, for example, hydrogenation steps, hydroisomerization steps, hydrocracking steps and combinations thereof.

A C<sub>1-2</sub> fraction can also be isolated from the Fischer-Tropsch synthesis and recycled upstream of a syngas generation process, flared, used to produce hydrogen, and/or used for fuel. A C<sub>3</sub>-enriched fraction, including more than 5% by weight C<sub>3</sub>, preferably more than 20% by weight C<sub>3</sub> and most preferably more than 40% by weight C<sub>3</sub> can also be obtained. This fraction can be recycled upstream of a syngas generation process, flared, used for fuel, transported in pressurized tankers, and/or transported in refrigerated tankers.

In one embodiment, petroleum products such as crude oil fractions with boiling points in the 650°F- or 650°F+ ranges can be blended with the corresponding 650°F- or 650°F+ containing fractions. The blending can occur at any site - the remote Fischer-Tropsch site, the lube manufacturing site, the distillate refining site or another location.

In a preferred process and business method embodiments, at least some portions of the syngas generator, Fischer-Tropsch synthesis reactor and/or equipment used for isolating the 650°F- or 650°F+ containing fractions can be disassembled, transported to another location, and used in the other location for performing the process described herein. Ideally, the parts can either be reassembled at the other location, or combined with other parts and assembled into a syngas generator, Fischer-Tropsch synthesis

reactor and/or equipment for isolating various product fractions. This embodiment is commercially relevant when considering the commercial lifetimes of remote gas sources.

### Detailed Description of the Invention

5

10

15

20

25

30

Preferred embodiments are now described as non-limiting illustrations of the claimed invention. A process for manufacturing a lube base stock, and the lube base stock produced by the process, is disclosed. The method involves converting a light hydrocarbon feedstock into syngas, converting the syngas to hydrocarbon products via Fischer-Tropsch synthesis, and isolating a predominantly 650°F- containing fraction (preferably including predominantly C<sub>5-20</sub> hydrocarbons) and a predominantly 650°F+ containing fraction either derived from, or, preferably, directly from the Fischer-Tropsch product stream. The 650°F- containing fraction can be converted to distillate fuels, either at the site where the Fischer-Tropsch synthesis occurs, or at a different location. The 650°F+ containing fraction is transported, received, and converted to lube base stocks, preferably at a site different from the site where the Fischer-Tropsch synthesis occurs. The fractions can be converted to distillate fuel and lube base stocks at the same site or at different sites. Fractions from multiple sites can be combined for conversion.

The following definitions will be helpful in understanding the compositions and methods described herein.

Linear hydrocarbon: The class of compounds including linear paraffins, linear olefins (internal and alpha), linear alcohols, and linear acids. A predominantly linear hydrocarbon fraction i.e. product, contains more than about 50 wt% linear hydrocarbons. Members of this class of compounds above C<sub>20</sub>, either singly or in mixtures, are typically solid or waxy at ambient temperature (20°C). The content of linear paraffins in materials lighter than about C<sub>20</sub> can be determined, for example, by gas chromatography. Since heavy linear paraffins are mostly solid materials, the content of linear hydrocarbons heavier than about C<sub>20</sub> can be determined by measuring the wax precipitated in the presence of methyl-ethylketone and toluene. An acceptable method involves the following: A 300-g portion of sample is dissolved in 1200 ml of 1:1 toluene-MEK solvent. Heating may be necessary to achieve complete dissolution.

5

10

15

20

25

30

The solution is then cooled overnight at -15 to -20°F to crystallize the wax. The wax crystals formed are filtered and recovered. The filtrate is vacuum distilled to separate the toluene-MEK solvent from the dewaxed oil. Occluded solvent in the wax is removed by heating the wax on a hot plate with nitrogen blowing on the surface. The weights of the recovered oil and wax are divided by the original sample weight to obtain the percent oil and wax.

Transportation temperature: For materials that are fluid at ambient temperature (20°C) or below, the transportation temperature is 20°C. For materials that are solid at typical ambient temperature, the transportation temperature is 5°C above the pour point, preferably 10°C above the pour point, and most preferably 20°C above the pour point as measured by ASTM D-97.

Remote site: A remote site is a location away from a refinery or market and which may have a higher cost of construction than the cost of construction at the refinery or market. In quantitative terms, the distance between the remote site and the refinery or market (the distance of transportation) is at least 100 miles, preferably more than 500 miles, and most preferably more than 1000 miles.

Transporting in liquid form: This means that at least a portion of the product is liquid, while the remainder can be solid. The portion that is liquid is at least 10%, preferably more than 25%, and most preferably more than 50%. It is within the scope of the methods described herein that waxy products will be completely liquid (or at least a pumpable slurry) upon initial loading in a transportation vessel and upon unloading the vessel, but at least a portion may become solid during transportation as the product cools. This solid can easily be melted at the receiving end, for example, using steam heaters. However, it is most preferable that the compositions are pumpable when loaded and unloaded, and that the product does not become completely solid during transportation.

Light hydrocarbon feedstock: These feedstocks can include methane, ethane, propane, butane and mixtures thereof. In addition, carbon dioxide, carbon monoxide, ethylene, propylene and butenes may be present.

Syncrude: A mixture derived from a Fischer-Tropsch process that does not meet all specifications for a finished salable product such as jet fuel, diesel fuel, lube base stock, fully refined wax, gasoline and the like without further processing.

Although syncrude has been described in the prior art as a  $C_5+$  containing material, syncrude, as used herein, refers to a 650°F+ containing stream, which preferably includes a relatively large amount of  $C_{36}+$  hydrocarbons (i.e., preferably greater than 10% by weight, more preferably greater than 20% by weight, and most preferably greater than 30% by weight). The  $C_{36}+$  hydrocarbons tend to form lube base stocks with relatively high viscosity, i.e., bright stocks.

5

10

15

20

25

30

Transportation method: The transportation method can vary, but preferably involves using a closed vessel with no significant exposure to air during transportation. At the temperature at which the compositions are transported, the pressure inside the vessel should not exceed about 14.9 psia.

Marine tanker: A ship used for transporting hydrocarbons, typically but not limited to crude oil, waxes and refined products.

Direct liquid product of a Fischer-Tropsch reactor: The direct liquid product is a liquid effluent from a Fischer-Tropsch reactor at reactor conditions. It will typically form a solid upon cooling to 20°C.

Direct vapor product of a Fischer-Tropsch reactor: The direct vapor product is a vapor effluent from a Fischer-Tropsch reactor at reactor conditions.

650°F+ containing product stream (e.g. fraction): A product stream that includes greater than 25% by weight 650°F+ material, preferably greater than 50% by weight 650°F+ material, and, most preferably, greater than 75% by weight 650°F+ material as determined by ASTM D2887 or other suitable methods. The 650°F- containing product stream is similarly defined.

Paraffin: A hydrocarbon with the formula  $C_nH_{2n+2}$ .

Olefin. A hydrocarbon with at least one carbon-carbon double bond.

Oxygenate: A hydrocarbonaceous compound that includes at least one oxygen atom.

Distillate fuel: A material containing hydrocarbons with boiling points between about 60 and 1100°F. The term "distillate" means that typical fuels of this type can be generated from vapor overhead streams from distilling petroleum crude. In contrast, residual fuels cannot be generated from vapor overhead streams by distilling petroleum crude, and are then a non-vaporizable remaining portion. Within the broad category of distillate fuels are specific fuels that include: naphtha, jet fuel, diesel fuel, kerosene,

aviation gas, fuel oil, and blends thereof.

Diesel fuel: A material suitable for use in diesel engines and conforming to at least one of the following specifications:

- ASTM D 975 "Standard Specification for Diesel Fuel Oils"
- European Grade CEN 90

5

10

15

20

25

- Japanese Fuel Standards JIS K 2204
- The United States National Conference on Weights and Measures (NCWM)
   1997 guidelines for premium diesel fuel
- The United States Engine Manufacturers Association recommended guideline for premium diesel fuel (FQP-1A)

Jet fuel: A material suitable for use in turbine engines for aircraft or other uses meeting at least one of the following specifications:

- ASTM D1655
- DEF STAN 91-91/3 (DERD 2494), TURBINE FUEL, AVIATION,
   KEROSINE TYPE, JET A-1, NATO CODE: F-35.
- International Air Transportation Association (IATA) Guidance Materials for Aviation, 4<sup>th</sup> edition, March 2000.

Gasoline: A material suitable for use in spark-ignition internal-combustion engines for automobiles and light trucks (motor gasoline) and in piston engine aircraft (aviation gasoline) meeting the current version of at least one of the following specifications:

Lube Base stock: A material meeting the definition in API 1509.

Fully refined wax: Fully refined wax meets FDA food grade requirements as defined in Title 21 of the Code of Federal Regulations, Sections 178.3710 and 172.886. Fully refined waxes have very low odor (ASTM D1833), oil content less than 0.5% (ASTM D721), and a Saybolt color of +25 to +30 (ASTM D156).

Natural gas is an example of a light hydrocarbon feed. In addition to methane, natural gas includes some heavier hydrocarbons (mostly C<sub>2-5</sub> paraffins) and other impurities, e.g., mercaptans and other sulfur-containing compounds, carbon dioxide, nitrogen, helium, water and non-hydrocarbon acid gases. Natural gas fields also

typically contain a significant amount of C<sub>5</sub>+ material, which is liquid at ambient conditions.

The methane, and optionally ethane and/or other hydrocarbons can be isolated and used to generate syngas. Various other impurities can be readily separated. Inert impurities such as nitrogen and helium can be tolerated. The methane in the natural gas can be isolated, for example in a demethanizer, and then de-sulfurized and sent to a syngas generator.

5

10

15

20

25

30

Methane (and/or ethane and heavier hydrocarbons) can be sent through a conventional syngas generator to provide synthesis gas. Typically, synthesis gas contains hydrogen and carbon monoxide, and may include minor amounts of carbon dioxide, water, unconverted light hydrocarbon feedstock and/or various other impurities. The presence of sulfur, nitrogen, halogen, selenium, phosphorus and arsenic contaminants in the syngas is undesirable. For this reason, it is preferred to remove sulfur and other contaminants from the feed before performing the Fischer-Tropsch chemistry or other hydrocarbon synthesis. Means for removing these contaminants are well known to those of skill in the art. For example, ZnO guardbeds are preferred for removing sulfur impurities. Means for removing other contaminants are well known to those of skill in the art.

The Fischer-Tropsch reaction may be effected in a fixed bed, in a slurry bed, or in a fluidized bed reactor. The Fischer-Tropsch reaction conditions may include using a reaction temperature of between 190°C and 340°C, with the actual reaction temperature being largely determined by the reactor configuration. Thus, when a fluidized bed reactor is used, the reaction temperature is preferably between 300°C and 340°C; when a fixed bed reactor is used, the reaction temperature is preferably between 200°C and 250°C; and when a slurry bed reactor is used, the reaction temperature is preferably between 190°C and 270°C.

An inlet synthesis gas pressure to the Fischer-Tropsch reactor of between 1 and 50 bar, preferably between 15 and 50 bar, may be used. The synthesis gas may have a H<sub>2</sub>:CO molar ratio, in the fresh feed, of 1.5:1 to 2.5:1, preferably 1.8:1 to 2.2:1. The synthesis gas typically includes 0.1 wppm of sulfur or less. A gas recycle may optionally be employed to the reaction stage, and the ratio of the gas recycle rate to the fresh synthesis gas feed rate, on a molar basis, may then be between 1:1 and 3:1,

5

10

15

20

25

30

preferably between 1.5:1 and 2.5:1. A space velocity, in m<sup>3</sup> (kg catalyst)<sup>-1</sup>hour<sup>-1</sup>, of from 1 to 20, preferably from 8 to 12, may be used in the reaction stage.

In principle, an iron-based, a cobalt-based or an iron/cobalt-based Fischer-Tropsch catalyst can be used in the Fischer-Tropsch reaction stage, although Fischer-Tropsch catalysts operated with high chain growth probabilities (i.e., alpha values of 0.8 or greater, preferably 0.9 or greater, more preferably, 0.925 or greater) are preferred. Reaction conditions are preferably chosen to minimize methane formation. This tends to provide product streams which mostly include wax and heavy products, i.e., largely paraffinic C<sub>20</sub>+ linear hydrocarbons.

The iron-based Fischer-Tropsch catalyst may include iron and/or iron oxides which have been precipitated or fused. However, iron and/or iron oxides which have been sintered, cemented, or impregnated onto a suitable support can also be used. The iron should be reduced to metallic Fe before the Fischer-Tropsch synthesis. The iron-based catalyst may contain various levels of promoters, the role of which may be to alter one or more of the activity, the stability, and the selectivity of the final catalyst.

Preferred promoters are those influencing the surface area of the reduced iron ("structural promoters"), and these include oxides or metals of Mn, Ti, Mg, Cr, Ca, Si, Al, or Cu or combinations thereof.

The products from Fischer-Tropsch reactions generally include a gaseous reaction product and a liquid reaction product. The gaseous reaction product includes hydrocarbons boiling below about 650°F (e.g., methane through middle distillates). The liquid reaction product includes hydrocarbons boiling above about 650°F (e.g., vacuum gas oil through heavy paraffins).

If the Fischer-Tropsch unit operates in the slurry mode, which typically has a liquid product phase present in the reactor under the reaction conditions, both the direct vapor and direct liquid products can be produced. The direct liquid product can be a 650°F+ containing product. Likewise the direct vapor product can be cooled to condense a 650°F+ containing product. Alternatively, the products from any type of Fischer-Tropsch unit can be combined, and separated, for example, by distillation to yield 650°F+ and 650°F- containing products.

The minus 650°F product can be separated into a tail gas fraction and a condensate fraction, i.e., about C<sub>5</sub> to C<sub>20</sub> normal paraffins and higher boiling

hydrocarbons, using, for example, a high pressure and/or lower temperature vaporliquid separator or low pressure separators or a combination of separators. The fraction boiling above about 650° primarily contains C<sub>20</sub> to C<sub>50</sub> linear paraffins with relatively small amounts of higher boiling branched paraffins.

5

A C<sub>1-2</sub> fraction can also be isolated and recycled upstream of a syngas generation process, flared, used to produce hydrogen and/or used for fuel. A C<sub>3</sub>-enriched fraction, including more than 5% by weight C<sub>3</sub>, preferably more than 20% by weight C<sub>3</sub> and most preferably more than 40% by weight C<sub>3</sub>, can also be obtained. This fraction can be recycled upstream of a syngas generation process, flared, used for fuel, transported in pressurized tankers, and/or transported in refrigerated tankers.

10

15

20

An LPG fraction can also be isolated. The LPG fractions preferably include mostly C<sub>3-5</sub> hydrocarbons, and preferably include mostly propane, n-butane and isobutane. They may also contain small amounts of pentanes and, less preferably, C<sub>3-5</sub> olefins, In a preferred embodiment, the LPG is a primary propane-rich and/or butane-rich product stream as such streams are known in the art. It is suitable for all possible end uses, for example, as an alternative fuel source for automobiles. Most preferably, the composition falls within the stringent specifications for LPG product streams in conventional LPG fuel use and in the area of alternative fuels. The LPG fraction may include an appreciable amount of olefins and/or oxygenates, which may be hydrotreated to form paraffins. In a preferred LPG product, the amount of ethane is less than about five percent by volume of the mixture, propylene is less than about one percent by volume of butane. C<sub>5</sub>+ hydrocarbons are preferably less than about twenty five percent by volume of the mixture. The sulfur content is preferably less than about 150 ppm.

25

The LPG fraction can be transported at a temperature at which the volatility does not exceed commercial specifications (i.e., less than about 15 psia, preferably less than about 11 psia). LPG generally has a pressure of about 120 psia at ambient temperatures, so it must be cooled when shipped to meet these specifications unless it is shipped under pressure in commercial transportation means which do not have these specifications.

30

In one embodiment, individual propane and butane streams are isolated, rather than LPG. This can be accomplished, for example, by passing a mixture including C<sub>1-4</sub>

hydrocarbons through a demethanizer, deethanizer and a depropanizer.

5

10

15 -

20

25

30

Preferably, volatile hydrocarbons that would raise the pressure above 15 psia, more preferably above 11 psia, at the transportation temperature are removed from all fractions to be transported.

When the gaseous reaction product from the Fischer-Tropsch synthesis step is being cooled and various fractions collected, the first fractions collected tend to have higher average molecular weights than subsequent fractions. A  $C_{14-20}$  fraction can be obtained, and combined with the liquid reaction products to form a  $C_{14}$ + syncrude, by isolating the fraction while the gaseous reaction products are being cooled. A  $C_{14-20}$  fraction can also be obtained by distilling the  $C_{5-13}$  hydrocarbons from the  $C_{14}$ + products after the middle distillate fraction is collected.

The vapor pressure of the composition can be measured at the transportation temperature using techniques well known to those in the art. If the vapor pressure of the composition exceeds specifications at the transportation temperature, lower boiling hydrocarbons can be removed from the composition, for example via vacuum distillation or other suitable means known to those of skill in the art.

The 650°F+ and the 650°F- containing fractions, products derived from these fractions, and blends of these and other fractions can be isolated and transported, for example, to commercial refineries for additional processing, such as solvent dewaxing, catalytic dewaxing, hydrotreatment, light paraffin hydroisomerization and/or hydrocracking. At least one of the products is a syncrude product. The products can be transported using any commonly used means of transportation, including marine tankers, rail cars, pipelines, trucks, barges and combinations thereof. A preferred means of transportation is a marine tanker and, more preferably, each transportable product is either transported in a separate marine tanker or in separate zones within the same tanker. When transported by rail, truck, or barge, each transportable product is preferably transported either in a separate rail, truck or barge, or in separate zones for each transportable product within the same rail, truck or barge. Each zone within a means of transportation or each separate means of transportation should have the ability to control the temperature such that each product can meet the desired pressure specifications. Accordingly, the means of transportation should be able to cool any LPG fractions that are transported (or, alternatively, be able to safely handle elevated

pressures), maintain any 650°F- containing fractions at or around room temperature, and maintain the 650°F+ containing fractions at a temperature at which they are molten, at least while the product is being pumped into or out of the transportation means, which temperature is generally at least 5°C above the pour point, preferably at least 10°C above the pour point. If the materials are fluid at ambient temperature, the shipping temperature is preferably around ambient. The transportation temperature is preferably no greater than 250°C, more preferably less than 200°C, and most preferably, less than 150°C.

5

10

15

20

25

30

The 650°F+ containing fractions will be dewaxed in a conventional solvent dewaxing step to remove high molecular weight n-paraffins. This dewaxing can occur before or after the fractions are transported to commercial refineries, but preferably it is after transport as this minimizes the construction of facilities at remote sites. The recovered dewaxed product, or dewaxed oil, can be fractionated under vacuum to produce paraffinic lube base stock fractions of different viscosity grades, or blended directly with other lube base stock fractions.

Solvent Dewaxing to make Lube Base stocks has been used for over 70 years and is described, for example, in <u>Chemical Technology of Petroleum</u>, 3rd Edition, William Gruse and Donald Stevens, McGraw-Hill Book Company, Inc., New York, 1960, pages 567 to 570. The basic process involves

- mixing a waxy hydrocarbon stream with a solvent, typically comprising a ketone (such as methyl ethyl ketone or methyl iso-butyl ketone) and an aromatic (such as toluene),
- chilling the mixture to cause wax crystals to precipitate,
- separating the wax by filtration, typically using rotary drum filters,
- recovering the solvent from the wax and the dewaxed oil filtrate.

There have been refinements in solvent dewaxing since its inception. For example, Exxon's DILCHILL® dewaxing process involves cooling a waxy oil in an elongated stirred vessel, preferably a vertical tower, with a pre-chilled solvent that will solubilize at least a portion of the oil while promoting the precipitation of the wax. Waxy oil is introduced into the elongated staged cooling zone or tower at a temperature above its cloud point. Cold dewaxing solvent is incrementally introduced into the cooling zone along a plurality of points or stages while maintaining a high degree of

agitation therein to effect substantially instantaneous mixing of the solvent and wax/oil mixture as they progress through the cooling zone, thereby precipitating at least a portion of the wax in the oil. DILCHILL® dewaxing is discussed in greater detail in the U.S. Pat. Nos. 4,477,333, 3,773,650 and 3,775,288. Texaco also has developed refinements in the process. For example, U.S. Patent No. 4,898,674 discloses how it is important to control the ratio of methyl ethylketone (MEK) to toluene and to be able to adjust this ratio, since it allows use of optimum concentrations for processing various base stocks. Commonly, a ratio of 0.7:1 to 1:1 may be used when processing bright stocks; and a ratio of 1.2:1 to about 2:1 may be used when processing light stocks.

5

10

15

20

25

30

The solvent dewaxed fraction can optionally be subjected to catalytic dewaxing, as described in more detail below.

The 650°F+ containing fractions can also be dewaxed in a catalytic dewaxing step to remove high molecular weight n-paraffins, in addition to or in place of solvent dewaxing. This dewaxing can also occur before or after the fractions are transported to commercial refineries but preferably it is after transport as this minimizes the construction of facilities at remote sites.

Catalytic Dewaxing consists to two main classes (Conventional Hydrodewaxing and Hydroisomerization Dewaxing), and Hydroisomerization Dewaxing can be further subdivided into Partial and Complete Hydroisomerization Dewaxing. All classes involve passing a mixture of a waxy hydrocarbon stream and hydrogen over a catalyst that contains an acidic component to convert the normal and slightly branched isoparaffins in the feed to other non-waxy species and thereby generate a lube base stock product with an acceptable pour point. Typical conditions for all classes involve temperatures from about 400 to 800°F, pressures from about 200 to 3000 psig, and space velocities from about 0.2 to 5 hr-1. The method selected for dewaxing a feed typically depends on the product quality, and the wax content of the feed, with Conventional Hydrodewaxing generally preferred for low wax content feeds. The method for dewaxing can be effected by the choice of the catalyst. The general subject is reviewed by Avilino Sequeira, in Lubricant Base Stock and Wax Processing, Marcel Dekker, Inc pages 194-223. The determination of the class of Dewaxing Catalyst among Conventional Hydrodewaxing, Partial Hydroisomerization Dewaxing and Complete Hydroisomerization dewaxing can be made by using the n-hexadecane

isomerization test as describe by Santilli et al. in U.S. Patent No. 5,282,958. When measured at 96% n-hexadecane conversion under conditions described by Santilli et al, Conventional Hydrodewaxing Catalysts will exhibit a selectivity to isomerized hexadecanes of less than 10%, Hydroisomerization Dewaxing Catalysts will exhibit a selectivity to isomerized hexadecanes of greater than or equal to 10%, Partial Hydroisomerization Dewaxing Catalysts will exhibit a selectivity to isomerized hexadecanes of greater than 10% to less than 40%, and Complete Hydroisomerization Dewaxing Catalysts will exhibit a selectivity to isomerized hexadecanes of greater than or equal to 40%, preferably greater than 60%, and most preferably greater than 80%.

10

15

20

5

Conventional Hydrodewaxing is defined for purposes of this document as a Catalytic Dewaxing process that uses a Conventional Hydrodewaxing Catalyst. In Conventional Hydrodewaxing, the pour point is lowered by selectively cracking the wax molecules, mostly to smaller paraffins boiling between propane and about octane. Since this technique converts the wax to less valuable by-products, it is useful primarily for dewaxing oils that do not contain a large amount of wax. Waxy oils of this type are frequently found in petroleum distillate from moderately waxy crudes (Arabian, North Slope, etc). Catalysts that are useful for Conventional Hydrodewaxing are typically 12ring zeolites and 10-ring zeolites. Zeolites of this class include ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-35, and Mordenite. Conventional Hydrodewaxing catalysts favor cracking in comparison to other method of conversion of paraffins. This is demonstrated by use of the n-hexadecane isomerization test by Santilli et al, in which Conventional Hydrodewaxing catalysts exhibit a selectivity to isomerized hexadecane products of less than 10%. In addition to the zeolites, metals may be added to the catalyst, primarily to reduce fouling. Representative process conditions, yields, and product properties for Conventional Hydrodewaxing are described, for example, U.S. Patent Nos. 4,176,050 to Chen et al., 4,181,598 to Gillespie et al., 4,222,855 to Pelrine et al., 4,229,282 to Peters et al., 4,211,635 to Chen, by Sequeira in the section titled "The Mobil Lube Dewaxing Process", pages 198-204 and references therein, J.D. Hargrove, G.J. Elkes, and A.H. Richardson, Oil and Gas J., p. 103, Jan. 15, 1979; the contents of each of which is incorporated herein by reference in their entirety.

30

25

Hydroisomerization Dewaxing is defined for purposes of this document as a Catalytic Dewaxing process that uses a Hydroisomerization Dewaxing Catalyst.

5

10

15

20

25

30

Hydroisomerization Dewaxing converts at least a portion of the wax to non-waxy isoparaffins by isomerization, while at the same time minimizing the conversion by cracking. When Conventional Hydrodewaxing and Hydroisomerization Dewaxing are compared on the same feed, the conversion of wax to non-waxy iso-paraffins during Hydroisomerization Dewaxing gives benefits of reducing the yield of less valuable byproducts, increasing the yield of lube oil, and generating an oil with higher VI and greater oxidation and thermal stability. Hydroisomerization Dewaxing uses a dualfunctional catalyst consisting of an acidic component and a metal component. Both components are required to conduct the isomerization reaction. Typical metal components are platinum or palladium, with platinum most commonly used. The choice and the amount of metal in the catalyst is sufficient to achieve greater than 10% isomerized hexadecane products in the test described by Santilli et al. When the selectivity for hexadecane isomers following Santilli's test exceed 40%, the catalyst is a Complete Hydroisomerization Dewaxing Catalyst. Since Hydroisomerization Dewaxing converts wax to iso-paraffins which boil in the lube base stock range, it is useful for dewaxing oils that contain a large amount of wax. Waxy oils of this type are obtained from slack waxes from solvent dewaxing processes, and distillates from highly waxy crudes (Minas, Altamont, etc.) and products from the Fischer Tropsch Process.

Partial Hydroisomerization Dewaxing is defined for purposes of this document as a Catalytic Dewaxing process that uses a Partial Hydroisomerization Dewaxing Catalyst. In Partial Hydroisomerization Dewaxing a portion of the wax is isomerized to iso-paraffins using catalysts that can isomerize paraffins selectively, but only if the conversion of wax is kept to relatively low values (typically below 50%). At higher conversions, wax conversion by cracking becomes significant, and yield losses of lube base stock becomes uneconomical. The acidic catalyst components useful for Partial Hydroisomerization Dewaxing include amorphous silica aluminas, fluorided alumina, and 12-ring zeolites (such as Beta, Y zeolite, L zeolite). Because the wax conversion is incomplete, Partial Hydroisomerization Dewaxing must be supplemented with an additional dewaxing technique, typically Solvent Dewaxing, Complete Hydroisomerization Dewaxing, or Conventional Hydrodewaxing in order to produce a lube base stock with an acceptable pour point (below about +10°F or -12°C). The wax

recovered from a solvent dewaxing operation following a Partial Hydroisomerization Dewaxing can be recycled to the Partial Hydroisomerization Dewaxing step.

Representative process conditions, yields, and product properties for Partial Hydroisomerization Dewaxing are described, for example, U.S. Patent Nos. 5,049,536 to Belussi et al.; 4,943,672 to Hamner et al., and EP 0 582 347 to Perego et al., EP 0 668 342 to Eilers et al, PCT WO 96/26993 by Apelian et al.; PCT WO 96/13563 by Apelian et al; the contents of each of which is incorporated herein by reference in their entirety.

5

10

15

20

25

30

Complete Hydroisomerization Dewaxing is defined for purposes of this document as a Catalytic Dewaxing process that uses a Complete Hydroisomerization Dewaxing Catalyst. In Complete Hydroisomerization Dewaxing, Complete Hydroisomerization Dewaxing Catalysts are used which can achieve high conversion levels of wax while maintaining acceptable selectivities to isomerization. Since wax conversion can be complete, or at least very high, this process typically does not need to be combined with additional dewaxing processes to produce a lube base stock with an acceptable pour point. Representative process conditions, yields, and product properties for Complete Hydroisomerization Dewaxing are described, for example, in U.S. Patent Nos. 5,135,638 to Miller, 5,246,566 to Miller; 5,282,958 to Santilli et al.; 5,082,986 to Miller; 5,723,716 to Brandes et al; the contents of each of which is incorporated herein by reference in their entirety.

Solvent dewaxing and catalytic dewaxing can still leave behind trace waxes. The presence of undesired wax can be detected by visual inspection, or using analytical techniques, for example light-scattering turbidity measurement as described in U.S. Patent No. 4,627,901.

Various methods have been developed for removing these trace contaminants. For example, U.S. Patent No. 4,950,382 discloses using adsorbents to remove wax. U.S. Patent Nos. 4,702,817 and 4,820,400 disclose performing electrophoresis on the hydrocarbons during solvent dewaxing.

The contents of each of these patents is hereby incorporated herein by reference in their entirety.

The fractions described above can optionally be combined with hydrocarbons

from other streams, although such hydrocarbons should not elevate the pressure of the composition above about 14.7 psia at the transportation temperature. For example, an LPG can be supplemented with LPG obtained from a natural gas field. Either fraction can be combined with a similar fraction obtained from the fractional distillation of crude oil or products derived therefrom. For example, the 650°F+ containing fraction can be combined with waxy crude oils and/or slack waxes from petroleum deoiling and dewaxing operations.

The 650°F+ and the 650°F- containing fractions, products derived from these fractions, and blends of these and other fractions can be subjected to hydroprocessing conditions. The hydroprocessing conditions include, for example, hydrotreatment, hydroisomerization dewaxing and/or hydrocracking. Olefins and oxygenates are hydrotreated to form paraffins. Paraffins in the C<sub>4-20</sub> range, preferably the C<sub>4-6</sub> range, are subjected to light paraffin hydroisomerization conditions to form isoparaffins. Hydrocarbons with chain lengths above a desired value, for example, C<sub>40</sub>, are hydrocracked. A C<sub>5-20</sub> product stream, including a mixture of paraffins and isoparaffins, can be isolated, for example, from the 650°F+ and/or the 650°F- containing fractions, although the 650°F+ containing fractions are preferably converted primarily to lube base stocks.

As used herein, "hydrotreating" or "hydrotreatment" is given its conventional meaning and describes processes that are well known to those skilled in the art.

Hydrotreating refers to a catalytic process, usually carried out in the presence of free hydrogen, in which the primary purpose is the desulfurization and/or denitrification of the feedstock. The sulfur is generally converted to hydrogen sulfide, and the nitrogen is generally converted to ammonia, and these can be removed from the product stream using means well known to those of skill in the art, including stripping and distillation. When hydrotreating is applied to Fischer-Tropsch stocks, the primary purpose is typically the saturation of olefins and deoxygenation of the feedstock. The oxygen in the oxygenates is converted to water, which can be removed from the product stream using means well known to those of skill in the art, including stripping and distillation. Typical hydrotreating conditions for petroleum and Fischer-Tropsch feedstocks vary over a wide range. In general, the overall liquid hourly space velocity (LHSV) is about 0.25 to 5.0, preferably about 0.5 to 2.0. The hydrogen partial pressure is greater than

200 psia, preferably ranging from about 500 psia to about 2000 psia. Hydrogen recirculation rates are typically greater than 50 SCF/Bbl, and are preferably between 300 and 5000 SCF/Bbl. Temperatures range from about 300°F to about 750°F, preferably ranging from 450°F to 750°F.

5

10

15

20

25

30

As used herein, "light paraffin hydroisomerization" refers to processes which isomerize at least a portion of the light normal paraffins to form isoparaffins. It is distinct from Hydroisomerization Dewaxing. This process is typically used to increase the octane rating of light naphthas or to manufacture iso-butane for alkylation. Typical light paraffin hydroisomerization conditions are well known in the literature and can vary widely. Isomerization processes are typically carried out at a temperature between 200°F and 700°F, preferably 300°F to 550°F, with a LHSV between 0.1 and 2, preferably between 0.25 and 0.50. Hydrogen is employed such that the mole ratio of hydrogen to hydrocarbon is between 1:1 and 5:1. Catalysts useful for isomerization processes are generally bifunctional catalysts that include a dehydrogenation/hydrogenation component and an acidic component. Preferably, these are combinations of zeolites and noble metals.

As used herein, "hydrocracking" refers to cracking hydrocarbon chains to form smaller hydrocarbons. This is generally accomplished by contacting hydrocarbon chains with hydrogen under increased temperature and/or pressure in the presence of a suitable hydrocracking catalyst. Hydrocracking catalysts with high selectivity for middistillate products are known.

More than one catalyst type may be used in the hydroprocessing step. The different catalyst types can be separated into layers or mixed. The hydroprocessing conditions can be varied depending on the fractions derived from the hydrocarbon synthesis step. For example, if the fractions include predominantly C<sub>20</sub>+ hydrocarbons, the hydroprocessing conditions can be adjusted to hydrocrack the fraction and provide predominantly C<sub>5-20</sub> hydrocarbons. A predominantly C20+ hydrocarbon or fraction is a fraction that includes at least 80%, preferably at least 85%, and more preferably, greater than 90% by weight of products that boil above 650°F. There is likely to be some degree of overlap between the fractions. If the fractions include predominantly C5-20 hydrocarbons, the hydroprocessing conditions can be adjusted to minimize hydrocracking. Those of skill in the art know how to modify reaction conditions to

adjust amounts of hydrotreatment, hydroisomerization, and hydrocracking.

5

10

15

20

25

30

Suitable catalysts and conditions are described, for example, in U.S. Patent No. 6,075,061, the contents of which are hereby incorporated by reference in its entirety. Other catalysts are described below.

Hydrotreating may also be used as a final step in the lube base stock manufacturing process. This final step, commonly called hydrofinishing, removes traces of aromatics, olefins, color bodies, and solvents. Clay treating to remove these impurities is a possible additional or alternative final process step.

Examples of hydrotreating catalysts which can be used in this embodiment are well known in the art. See, for example, U.S. Patent Nos. 4,347,121 and 4,810,357 for general descriptions of hydrotreating, and typical catalysts used in hydrotreating processes.

Suitable catalysts include noble metals from Group VIIIA, such as platinum or palladium on an alumina or siliceous matrix, and unsulfided Group VIIIA and Group VIB metals, such as nickel-molybdenum or nickel-tin on an alumina or siliceous matrix. U.S. Pat. No. 3,852,207 describes a suitable noble metal catalyst and reaction conditions. Other suitable catalysts are described, for example, in U.S. Patent Nos. 4,157,294 and 3,904,513. Non-noble metals (such as nickel-molybdenum) are usually present in the final catalyst composition as oxides, or possibly as sulfides, when such compounds are readily formed from the particular metal involved. Preferred non-noble metal catalyst compositions contain in excess of about 5 weight percent, preferably about 5 to about 40 weight percent molybdenum and/or tungsten, and at least about 0.5, and generally about 1 to about 15 weight percent of nickel and/or cobalt determined as the corresponding oxides. The noble metal (such as platinum) catalysts include in excess of 0.01 percent metal, preferably between 0.1 and 1.0 percent metal. Combinations of noble metals may also be used, such as mixtures of platinum and palladium.

The hydrogenation components can be incorporated into the overall catalyst composition by any one of numerous procedures. The hydrogenation components can be added to matrix component by co-mulling, impregnation, or ion exchange and the Group VI components, i.e., molybdenum and tungsten can be combined with the refractory oxide by impregnation, co-mulling or co-precipitation. The matrix

5

10

15

20

25

30

component can be of many types including some that have acidic catalytic activity. Ones that have activity include amorphous silica-alumina or may be a zeolitic or nonzeolitic crystalline molecular sieve. Examples of suitable matrix molecular sieves include zeolite Y, zeolite X and the so-called ultra stable zeolite Y and high structural silica: alumina ratio zeolite Y such as that described in U.S. Patent Nos. 4,401,556, 4,820,402 and 5,059,567. Small crystal size zeolite Y, such as that described in U.S. Patent No. 5,073,530, can also be used. Non-zeolitic molecular sieves which can be used include, for example, silicoaluminophosphates (SAPO), ferroaluminophosphate. titanium aluminophosphate, and the various ELAPO molecular sieves described in U.S. Patent No. 4,913,799 and the references cited therein. Details regarding the preparation of various non-zeolite molecular sieves can be found in U.S. Patent Nos. 5.114.563 (SAPO); 4,913,799 and the various references cited in U.S. Patent No. 4,913,799. Mesoporous molecular sieves can also be used, for example the M41S family of materials (J. Am. Chem. Soc. 1992, 114, 10834-10843), MCM-41 (U.S. Patent Nos. 5,246, 689, 5,198,203 and 5,334,368), and MCM-48 (Kresge et al., Nature 359) (1992)710).

Suitable matrix materials may also include synthetic or natural substances as well as inorganic materials such as clay, silica and/or metal oxides such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-berylia, silica-titania as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia, and silica-magnesia zirconia. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays which can be composited with the catalyst include those of the montmorillonite and kaolin families. These clays can be used in the raw state as originally mined or initially subjected to calumniation, acid treatment or chemical modification.

Catalysts useful for isomerization processes are generally bifunctional catalysts that include a dehydrogenation/hydrogenation component, an acidic component, and optionally, but preferably, a hydrocracking suppressant. Preferably, the light paraffin hydroisomerization catalysts used herein are not sulfur sensitive but instead are enhanced by the presence of sulfur.

The light paraffin hydroisomerization catalyst(s) can be prepared using well known methods, e.g., impregnation with an aqueous salt, incipient wetness technique, followed by drying at about 125-150°C for 1-24 hours, calcination at about 300-500°C for about 1-6 hours, reduction by treatment with a hydrogen or a hydrogen-containing gas, and, if desired, sulfiding by treatment with a sulfur-containing gas, e.g., H<sub>2</sub>S at elevated temperatures. The catalyst will then have about 0.01 to 10 wt % sulfur. The metals can be composited or added to the catalyst either serially, in any order, or by co-impregnation of two or more metals. Additional details regarding preferred components of the light paraffin hydroisomerization catalysts are described below.

10

5

The dehydrogenation/hydrogenation component is preferably a Group VIII metal, more preferably a Group VIII non-noble metal, or a Group VI metal. Preferred metals include nickel, platinum, palladium, cobalt and mixtures thereof. The Group VIII metal is usually present in catalytically effective amounts, that is, ranging from 0.5 to 20 wt %. Preferably, a Group VI metal is incorporated into the catalyst, e.g., molybdenum, in amounts of about 1-20 wt %.

15

20

Examples of suitable acid components include crystalline zeolites, molecular sieves, catalyst supports such as halogenated alumina components or silica-alumina components, and amorphous metal oxides. Such paraffin isomerization catalysts are well known in the art. The acid component may be a catalyst support with which the catalytic metal or metals are composited. Preferably, the acidic component is a zeolite or a silica-alumina support, where the silica/alumina ratio (SAR) is less than 1 (wt./wt.).

25

Preferred supports include silica, alumina, silica-alumina, silica-alumina-phosphates, titania, zirconia, vanadia and other Group III, IV, V or VI oxides, as well as Y sieves, such as ultra stable Y sieves. Preferred supports include alumina and silica-alumina, more preferably silica-alumina where the silica concentration of the bulk support is less than about 50 wt %, preferably less than about 35 wt %, more preferably 15-30 wt %. When alumina is used as the support, small amounts of chlorine or fluorine may be incorporated into the support to provide the acid functionality.

30

A preferred supported catalyst has surface areas in the range of about 180-400 m<sup>2</sup>/gm, preferably 230-350 m<sup>2</sup>/gm, and a pore volume of 0.3 to 1.0 ml/gm, preferably

0.35 to 0.75 ml/gm, a bulk density of about 0.5-1.0 g/ml, and a side crushing strength of about 0.8 to 3.5 kg/mm.

The preparation of preferred amorphous silica-alumina microspheres for use as supports is described in Ryland, Lloyd B., Tamele, M. W., and Wilson, J. N., <u>Cracking Catalysts</u>. Catalysis, Volume VII, Ed. Paul H. Emmett, Reinhold Publishing Corporation, New York, (1960).

5

10

15

20

25

30

Hydrocracking catalysts are well known to those of skill in the art, and include catalysts described above that are not sensitive to the presence of sulfur. In the absence of sulfur, such hydrocracking catalysts may produce significant  $C_{1-4}$  fractions, which are undesirable. Suppression of these fractions can be enhanced by using a hydrocracking suppressant. Suitable hydrocracking suppressants include Group IB metals, e.g., preferably copper, more preferably, in amounts of about 0.1-10 by weight of total catalyst, sulfur-containing organic compounds and pre-sulfided catalysts

Some acidic components also function as well as a hydrocracking suppressants, particularly if they are pre-sulfided catalysts. Catalysts may be pre-sulfided using known methods, for example, by treatment with hydrogen sulfide until breakthrough occurs. Catalysts containing sulfur typically have at least about 0.01 wt % sulfur, preferably about 0.01 to 20% sulfur, more preferably 0.1 to 10 wt %.

The hydroprocessing step(s) can use one or more additional hydrocracking suppressants. Examples of suitable hydrocracking suppressants include Group IB metals, sulfur and mixtures thereof. Pre-sulfided catalysts are preferred hydrocracking suppressants.

If the feedstocks to the Catalytic Dewaxing, Light Paraffin Hydroisomerization, and other sulfur-sensitive processes include sulfur-containing compounds, then sulfur removal is necessary for process efficiency. Since the syngas for an Fischer Tropsch process is typically essentially sulfur-free, no appreciable amount of sulfur is likely to come from the Fischer-Tropsch products, although oxygenates are often formed. However, sulfur and other heteroatoms may be introduced by blending with other feedstreams, or in the hydroprocessing steps, for example, if pre-sulfided catalysts are used. Methods for removing heteroatom impurities are well known to those of skill in the art, and include, for example, extractive Merox, hydrotreating, adsorption, etc. Hydrotreating is the preferred means for removing these and other impurities.

Preferably, the equipment used in the syngas generation, Fischer-Tropsch synthesis and/or product isolation is capable of being transported, in whole or in part, from remote location to remote location, thereby saving capital expense when a natural gas source runs dry.

5

Moving a GTL (Gas-to Liquids) facility from one location to another can be accomplished, for example, by simply dismantling the GTL facility from its original location, isolating the equipment and then moving it. The most capital expensive items are most likely to be moved to the new location. These items include compressors, reactors, large pumps, high pressure vessels, control systems, software for control systems and other expensive items.

10

15

A preferred approach, however, is not to build a large integrated GTL facility for the production of syncrudes for lube production, but rather to build the GTL facility in readily transported modules. These modules can be built at a developed site where construction costs are relatively low, moved to the remote gas source, piped together, and operated to produce the syncrude. When the gas source is exhausted, at least some of modules can be moved to another remote gas source. The modules can be skid-mounted, which means that they are shipped by floating vessel and unloaded to shore and moved to their operating location. Alternatively, when the gas source is near a shore or river or other accessible location, the modules can be built on barges and moved to the near-shore location. The barges are secured by driving piles or by some other fashion, piped together, and operated to produce syncrude. Combinations of integrated facilities, skid mounted barges, and secured barges can also be used.

20

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. Such equivalents are intended to be encompassed by the following claims.

25

Additionally it is clearly contemplated as part of the claimed invention that the process sites remote from each other my be in different countries and still be within the scope and coverage of the inventions claimed embodiments.

# WHAT IS CLAIMED IS:

5

15

20

25

- 1. A process for manufacturing a lube base stock comprising:
  - a) converting a light hydrocarbon feed to syngas,
  - b) subjecting the syngas to Fischer-Tropsch synthesis to form a predominantly linear hydrocarbon product,
  - c) isolating a 650°F- containing fraction and a 650°F+ containing fraction from the predominantly linear hydrocarbon product,
  - d) transporting the 650°F+ containing fraction to a refinery, and
  - e) converting the 650°F+ containing fraction to a lube base stock.
- 2. The process of claim 1, wherein at least a portion of the 650°F- containing fraction is converted to a distillate fuel composition.
  - 3. The process of claim 1, wherein at least a portion of the 650°F- containing fraction is transported to a refinery and converted to a distillate fuel composition.
  - 4. The process of claim 1, wherein the 650°F+ containing fraction used in step d and/or e is isolated by condensing the direct vapor product of a Fischer-Tropsch reactor.
  - 5. The process of claim 1, wherein the 650°F+ containing fraction used in step d and/or e is the direct liquid product of a Fischer-Tropsch reactor.
  - 6. The process of claim 1, wherein the 650°F+ containing fraction used in step d and/or e is derived from the direct liquid product of a Fischer-Tropsch reactor.
  - 7. The process of claim 1, wherein the conversion in step e comprises dewaxing selected from the group consisting of: solvent dewaxing, catalytic dewaxing, and combinations thereof.
  - 8. The process of claim 1, wherein the conversion in step e comprises a hydrotreatment step.
  - 9. The process of claim 1, wherein the conversion step e is performed on a plurality of fractions obtained from a plurality of different locations.
  - 10. A process for manufacturing a lube base stock including at least one first site and at least one second site, remote from each other, wherein one or a plurality of said first sites form a product used at the said second site(s), said second site(s) forming the lube base stock, the process comprising:
    - a) receiving at the second site a 650°F+ containing fraction made by:

i) converting a light hydrocarbon feed to syngas,

5

25

- ii) subjecting the syngas to Fischer-Tropsch synthesis to form a predominantly linear hydrocarbon product, and
- iii) isolating a 650°F- containing fraction and a 650°F+ containing fraction from the product of the Fischer-Tropsch synthesis,
- b) converting the 650°F+ containing fraction to a lube base stock.
- 11. The process of claim 10, further comprising receiving at least a portion of the 650°F- containing fraction and converting a portion of said fraction to a distillate fuel composition.
- 12. The process of claim 10, wherein the 650°F+ containing fraction used in step iii) and/or iv) is isolated by condensing the direct vapor product of a Fischer-Tropsch reactor.
  - 13. The process of claim 10, wherein the 650°F+ containing fraction used in step iii) and/or iv) is the direct liquid product of a Fischer-Tropsch reactor.
- 14. The process of claim 10, wherein the 650°F+ containing fraction used in step iii) and/or iv) is derived from the direct liquid product of a Fischer-Tropsch reactor.
  - 15. The process of claim 10, wherein the conversion in step b comprises dewaxing selected from the group consisting of: solvent dewaxing, catalytic dewaxing, and combinations thereof.
- 20 16. The process of claim 10, wherein the conversion in step b comprises a hydrotreatment step.
  - 17. The process of claim 10, wherein the 650°F+ containing fraction of step a) is made by the process which further comprises:
    - a') setting up the Fischer-Tropsch synthesis plant at a first remote location, wherein the plant comprises a syngas generator, a Fischer-Tropsch reactor and equipment for isolating various products from the Fischer-Tropsch reactor, and wherein the first remote location has a natural gas source,
    - b') converting natural gas at the first remote location to syngas,
    - c') converting the syngas to 650°F+ containing fraction(s) via Fischer-Tropsch synthesis,
    - d') disassembling at least a portion of the equipment in step a'),

e') transporting at least a portion of those parts of d') to a second remote natural gas field, and

- f) assembling a Fischer-Tropsch synthesis plant at the second remote natural gas field comprising at least a portion the parts in step e').
- 18. The process according to claim 17 wherein the Fischer Tropsch synthesis plant of a') includes components that can be readily disassembled and reassembled.
  - 19. A process for receiving a Fischer-Tropsch product from converted natural gas, wherein the Fischer-Tropsch conversion is done at multiple remote locations, said process comprising:
    - a) receiving a product manufactured by:
      - i) setting up a plant at a first remote location, wherein the plant comprises a syngas generator, a Fischer-Tropsch reactor and equipment for isolating various products from the Fischer-Tropsch reactor, and wherein the first remote location has a natural gas source
      - ii) converting natural gas at the first remote location to syngas,
      - iii) converting the syngas to products via Fischer-Tropsch synthesis,
      - iv) disassembling at least a portion of the equipment in step i,
      - v) transporting the disassembled equipment to a second remote location,
      - vi) setting up a plant at the second remote location using the disassembled equipment in step d, and
      - vii) repeating steps ii) and iii), and
    - b) refining the received product.
- 20. A method for manufacturing hydrocarbon products from remote natural gas fields, comprising:
  - setting up a plant in a first remote natural gas field wherein the plant comprises components that can be readily disassembled and reassembled, and wherein the plant can convert natural gas to hydrocarbon products,
  - b) converting natural gas to hydrocarbon products at the first remote natural gas field until the supply of natural gas is substantially depleted,
  - c) disassembling those parts of the plant which can be readily disassembled,

15

20

d) transporting at least a portion of those parts of c) to a second remote natural gas field, and

e) assembling a plant at the second remote natural gas field comprising at least a portion the parts in step d).

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/45509

A. CLASSIFICATION OF SUBJECT MATTER  IPC(7) : C10G 47/02, 47/24; C07C 2/02, 7/20  US CL : 585/14, 518, 899; 208/108				
According to International Patent Classification (IPC) or to both national classification and IPC  B. FIELDS SEARCHED				
Minimum documentation searched (classification system followed by classification symbols) U.S.: 585/14, 518, 899; 208/108				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category *	Citation of document, with indication, where ap	opropriate, of the relevant passages	Relevant to claim No.	
x	US 5,968,991 A (MAULDIN) 19 October 1999, col. 5, lines 1-45		1-20	
Further documents are listed in the continuation of Box C.		See patent family annex.		
*A ** document defining the general state of the art which is not considered to be of particular relevance		date and not in conflict with the application of theory underlying the investigation of particular relevance; the	relevance; the claimed invention cannot be	
"B" carlier ap	pplication or patent published on or after the international filing date	considered novel or cannot be considered when the document is taken alone	red to involve an inventive step	
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		considered to involve an inventive ste combined with one or more other suc	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	
"O" document referring to an oral disclosure, use, exhibition or other means		-		
	t published prior to the international filing date but later than the late claimed	"&" document member of the same patent	гашцу	
		Date of mailing of the international search report  17 APR 2002		
20 February 2002 (20.02.2002)		Authorized officery		
Conditional of Facing and Fideward		Welter O. Delle Me		
Box PCT Washington, D.C. 20231				
Faccimile No. (703)305-3230		Telephone No. (703) 308-0661		